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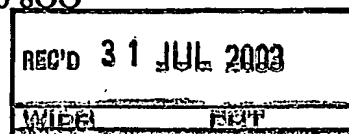
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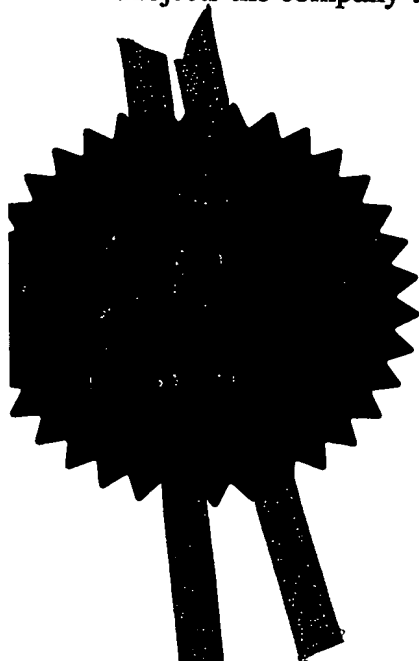


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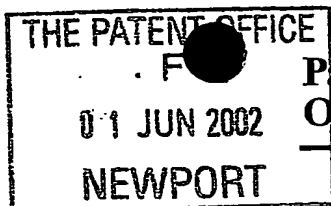


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Dated 8 July 2003

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# Request for grant of a patent

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1. Your reference	GW/MK/G32589		
2. Patent application number (The Patent Office will fill in this part)	0212848.6		F-1 JUN 2002
3. Full name, address and postcode of the or of each applicant ( <u>underline all surnames</u> )	Surface Innovations Limited  Redgate House Wolsingham County Durham DL13 3HH  8384703001 <i>TS</i> England		
Patents ADP number (if you know it)			
If the applicant is a corporate body, give the country/state of its incorporation			
4. Title of the invention	Introduction of Liquid/Solid Slurry into an Exciting Medium		
5. Name of your agent (if you have one)	Bailey Walsh & Co.		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	5, York Place Leeds LS1 2SD		
Patents ADP number (if you know it)	224001		
6. If you are declaring priority from one or more earlier patent applications, give the and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / years)
7. If this application is divided or otherwise derived from an earlier UK application, the earlier application	Number of earlier application	Date of filing (day / month / years)	
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer "Yes" if:	Yes		
a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body See note (d)			

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form

Description

11

Claim(s)

Abstract

Drawing(s)

2 x 2 SW

10. If you are also filing any of the following, state how many of each item.

Priority Documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (Please specify)

11. I/We request the grant of a patent on the basis of this application

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Date

31<sup>st</sup> May 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

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## Introduction of Liquid/Solid Slurry into an Exciting Medium

The invention of this application relates to the use of an atomiser to inject a liquid or liquid/solid slurry into an exciting medium to generate a resultant high flux of coating forming material which permits rapid deposition, even from involatile monomers to allow the formation of a coating.

It is known to use a means of monomer atomisation (typically an ultrasonic nozzle) to deposit coatings. Patent WO 9810116 includes examples which use relatively high powers ( $\sim 90$  W) that produce continuous plasma to create cross linked products with poor structural retention. For example, the polyHEMA coating created is amber coloured whereas a good quality coating would be expected to be translucent. Furthermore, the patent does not specify the use of a pulsed plasma.

The patent WO 0228548 refers only to atmospheric pressure plasmas and does not specify that the plasma is pulsed and indicates that retention of the chemical properties of the atomised liquid is an inevitable consequence of continuous high-rate deposition.

Both patents WO9738801 and WO9858117 describe the application of coatings. However, the latter does not mention the use of atomised liquid coating forming materials (all monomers are implicitly gaseous) and the former appears to specifically describe a two-step process. Thus, in both cases the deposition rate is slow and, as a result, commercial implementation problematical.

The aim of the present invention is to provide an improved method and system for the application of surface coatings which

allows the introduction of material into an excitation medium which, in turn, allows the application of higher quality coatings to substrates.

In a first aspect of the invention there is provided a method for depositing a coating onto a substrate, said method comprising the introduction of an atomised coating forming material into a pulsed exciting medium, the activated atomised coating forming material being deposited onto a substrate to form the coating on the substrate and characterised in that the exciting medium is pulsed.

The pulsing of the excitation medium results in the formation of coating that significantly retains the chemical properties of the atomised coating forming material introduced into the exciting medium. The use of the atomiser enables rapid deposition rates to be achieved even from low vapour pressure materials.

In one embodiment, additional materials are added to the flow of the atomised coating forming material. The additive materials act as buffers which can be required to maintain the process pressure and/or carry the atomised coating forming material.

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The additive materials can have the additional capacity to modify and/or be incorporated into the coating forming material and/or the resultant coating.

In one embodiment, the introduction of materials additional to the atomised coating forming material is pulsed.

In one embodiment the exciting medium is a pulsed plasma discharge which can be selectively operated at atmospheric, sub-atmospheric or low-pressure.

In one embodiment the pulsed plasma discharge generated by an alternating current voltage.

In another embodiment, the pulsed plasma is produced by audio-frequencies, radio-frequencies or microwave-frequencies.

In a yet further embodiment, the pulsed plasma is produced by direct current voltage.

Typically, wherein the exciting medium is created by a pulsed flux of electromagnetic radiation such as UV light or  $\gamma$ -radiation, or a pulsed flux of ionised particles such as ions, electrons or  $\alpha$ -radiation, or a pulsed flux of radicals, or by more than one of the means described whether singly in succession, in simultaneous combination, or in a succession of combinations.

Typically the substrate to which the coating material is applied is located substantially inside the pulsed exciting medium during coating deposition or alternatively is deposited onto a substrate located outside of the pulsed exciting medium. Thus avoiding excessive damage to the substrate or coating.

In a further aspect of the invention there is provided a method of producing a multi-layered coating on a substrate wherein the substrate is repeatedly exposed to excited coating forming material produced as herein described.

In one embodiment the composition of the precursor and/or the nature of the exciting medium are changed during the coating formation.

In one embodiment the substrate is coated continuously by use of a reel-to-reel apparatus, and/or the coating formed on the

substrate can be post-treated by exposure to an exciting medium and/or pre-treated prior to coating or a substrate with a previously applied coating by exposure to an exciting medium prior to coating deposition.

The substrate can comprise, but is not limited to: metal, glass, semiconductor, ceramic, polymer, woven or non-woven fibres, natural fibres, synthetic fibres, cellulosic material, and powder.

The coating forming material can constitute, but is not limited to, an organic, organosilicon, organometallic, or inorganic material, or mixtures thereof.

The coating can be selected to increase the hydrophobic and/or oleophobic, adhesive, gas barrier, moisture barrier, release, electrical and thermal conductivity, dielectric, optical or tribological properties of the substrate.

In one embodiment the atomiser is an ultrasonic nozzle supplied with coating forming material in the form of a liquid or liquid/solid slurry. The atomiser used can be a nebulizer supplied with coating forming material in the form of a liquid or liquid/solid slurry, and a carrier gas which may be inert or reactive. Alternatively the atomiser is a plain-jet gas blast atomiser supplied with coating forming material in the form of a powder, and a carrier gas which may be inert or reactive.

More than one atomiser can be used to supply coating forming material to the excitation medium.

If required, the excitation medium and surrounding apparatus are heated, and the coated substrate can be subject to subsequent derivatization by methods known in the art (e.g. tethering of biomolecules).

In a further aspect of the invention there is provided a method for depositing a coating formed from a liquid coating forming material (such as an organic or organo-silicon monomer or oligomers) or a liquid mixed with substantially insoluble particles (a liquid/solid slurry), said method comprising atomising or nebulizing the coating forming material and introducing it into a pulsed exciting medium (preferably a plasma) that facilitates the formation of activated precursor species to the coating (such as monomeric or oligomeric radicals and ions), these precursor species deposited onto a substrate, forming the coating.

The pulsing of the excitation medium produces coatings that retain the chemical properties of the atomised coating forming material to a far greater extent compared to the conventional non-pulsing counterpart. The use of an atomiser enables rapid deposition even from low vapour pressure materials.

In a preferred embodiment of the method, the coating forming material, either a liquid or liquid/solid slurry, is atomised by an ultrasonic nozzle into an excitation zone, heated to prevent condensation. Other means of atomising the coating forming material include, but are not limited to, nebulizers and plain-jet air blast atomizers.

In one embodiment, the exciting medium contains the atomised coating forming material in the absence of other materials or mixed with, for example, an inert or reactive gas. The additional material may be introduced into, prior to, or subsequent to the excitation chamber continuously or in a pulsed manner by way of, for example, a gas pulsing valve.



In a further aspect of the invention there is provided apparatus for the application of a coating to a substrate, said apparatus comprising a vacuum chamber, atomising means for introducing atomised coating forming material into the chamber, means for creating an exciting medium within the chamber, and a means for introducing and holding a substrate to be coated in the chamber, said atomising means directing the atomised coating forming material to pass through the exciting medium prior to reaching the substrate and characterised in that the means for creating the exciting medium is controlled so as to generate the exciting medium in a pulsed manner.

Specific examples of the invention is now described with reference to the accompanying drawings; wherein:-

Figures 1a and b, illustrate two embodiments, in schematic fashion, of the method of the invention; and

Figure 2 illustrates apparatus that uses a pulsed radio frequency plasma to effect deposition of atomised coating forming materials.

With reference to Figures 1a and b there is shown an atomiser 2, substrate 4, and exciting medium 6.

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The exciting medium 6 shall, in its preferred embodiments, constitute a pulsed plasma discharge ignited surrounding (Figure 1a), or in a region downstream of (Figure 1b), the source 2 of atomised coating forming material. Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by audiofrequencies, radiofrequencies (RF), microwaves or direct current. The plasma may operate at low-pressure, atmospheric or sub-atmospheric pressures as are known in the art. Of special utility are: low-pressure radio-

frequency plasmas wherein the gas pressure is 0.01 to 10 mbar and atmospheric-pressure-glow-discharges (APGDs) which typically utilise a high flux of carrier gas (usually helium or argon) and a high frequency power supply (1 kHz to RF).

Precise conditions under which pulsed plasma deposition can take place in an effective manner will vary depending upon factors such as the nature of the atomised coating forming material or the substrate and can be determined using routine methods. In general however, coating is effected by applying a pulsed high frequency voltage in a sequence that yields very low average powers for example of less than 10 W and preferably of less than 1 W. An example of such a sequence is one in which the power is on for 20  $\mu$ s and off for 20000  $\mu$ s.

The greater level of structural retention that pulsed plasma deposition results in can in many cases be attributed to free radical polymerisation occurring during the duty cycle off-time and less fragmentation and VUV/ion bombardment during the on-time.

Alternative pulsed means for exciting the atomised coating forming material prior to deposition include, but are not limited to: pulsed UV/VUV irradiation (using sources such as those manufactured by Xenon Corporation), pulsed ion beams, and pulsed electron beam treatment. Means of pulsing these excitation sources, in addition to electronic switching, include rotating shutters and grids possessing a modulated electrical bias capable of intermittently preventing the transit of appropriately charged species.

It is envisaged that multi-layer coatings may be produced by a variety of means: such as pulsing the atomisation source, pulsing the introduction of reactive, additive species to the excitation

medium (e.g. intermittently adding oxygen to a plasma); changing the location of substrate during coating; changing the duty cycle of the pulsed excitation medium (e.g. alternating between long and short plasma on times to produce alternating cross-linked and well-retained layers); changing the nature of the excitation medium (e.g. from pulsed plasma to pulsed UV); changing the composition of the coating forming material, and performing multiple treatments (with one or more apparatuses).

The invention will now be particularly described by way of example with reference to Figure 2 which shows a diagram of an apparatus that uses a pulsed radiofrequency plasma 106 to effect deposition of atomised coating forming materials 110 dispensed from atomiser 102 onto substrates 104.

The examples are intended to illustrate the present invention but are not intended to limit the same.

#### Example 1

##### Deposition of hydrophobic / oleophobic films

1H, 1H, 2H, 2H perfluorooctylacrylate is placed into monomer tubes 112 having been purified using repeated freeze-pump-thaw cycles. Coating deposition experiments are performed in an ~~apparatus consisting of ultrasonic atomisation nozzles 102~~ interfaced with a capacitively-coupled radiofrequency plasma reactor 106. A monomer tube is connected to each ultrasonic nozzle by way of a metering valve 114. The ultrasonic nozzle themselves are connected to the plasma-reactor by way of "nitrile" O-rings 116.

A "Pirani" pressure gauge is connected to the capacitively coupled plasma chamber. An inlet valve is connected with the external, ambient air supply and a butterfly valve leads to an

Edwards E2M28 two stage rotary pump by way of a liquid nitrogen cold trap 118. All connections are grease free.

An L-C matching unit and a power meter are used to couple the output from a 13.56 MHz RF generator 120 to the parallel electrodes 122, 124 that describe the plasma excitation volume 106. This arrangement minimises the standing wave ratio (SWR) of the power transmitted from the RF generator to the partially ionised gas in the plasma excitation volume. The plasma is pulsed by using a pulsed signal generator 126 to trigger the output from the RF generator and a cathode ray oscilloscope to monitor the pulse width and amplitude. The average power  $\langle P \rangle$  delivered to the system during pulsing is given by the following formula:

$$\langle P \rangle = P_{CW} \{ T_{on} / (T_{on} + T_{off}) \}$$

where  $T_{on} / (T_{on} + T_{off})$  is defined as the duty cycle and  $P_{CW}$  is the average continuous wave power.

Prior to the deposition of the coating forming material the ultrasonic nozzles, metering valves and related fittings are rinsed with propan-2-ol and air-dried. The monomer tube, ultrasonic nozzle, metering valve and related fittings are then attached to the plasma reactor which has been previously cleaned with a continuous RF oxygen plasma. Next the silicon substrates are placed onto the lower electrode of the plasma reactor and the apparatus evacuated to base pressure ( $2 \times 10^{-3}$  Torr).

The metering valves are then opened until the liquid monomer flows into the ultrasonic nozzles at a rate of  $8 \times 10^{-4} \text{ ml s}^{-1}$ . Switching on the ultrasonic generators (3.0 W) initiates atomisation of the coating forming material, resulting in an increase in the chamber pressure to 0.1 Torr. The pulsed plasma is then ignited. Typically a 0-10 minute deposition duration is used, and found to be sufficient to give complete

coverage of the substrate. After this the metering valve 114 is closed, the RF 120 and signed 126 generators switched off, and the apparatus evacuated before finally venting to atmospheric pressure.

A spectrophotometer (Aquila Instruments nkd-6000) is used to determine the thickness of the coatings. Contact angle measurements are made with a video capture apparatus (AST Products VCA2500XE) using sessile 2  $\mu$ L droplets of deionised water and n-decane as probe liquids for hydrophobicity and oleophobicity respectively.

Table 1 shows the results of 10 minutes of deposition onto silicon wafers in accordance with the method of this example where:

$$P_{\text{cov}} = 40 \text{ W}$$

$$T_{\text{on}} = 200 \text{ microseconds}$$

$$T_{\text{off}} = 10 \text{ milliseconds}$$

Table 1

Coating Forming Material	Deposition Duration /min	Film Thickness /nm	Contact Angle /°	
			Water	Decane
1H, 1H, 2H, 2H perfluorooctylacrylate	8	680	128	74°

In Table 1 it can be seen that the method of the invention enables the rapid pulsed plasma deposition of thick films from a monomer possessing low volatility. The water contact angle results confirm that the films are hydrophobic and the decane

contact angles are indicative of a good degree of oleophobicity (and hence structural retention).

### Example 2

#### Deposition of a hydrophilic coating

In a second illustrative example the method and apparatus of Example 1 above are repeated using 2-hydroxyethyl methacrylate as the coating forming material. In this case, the conditions were:

$$P_{\text{cw}} = 40 \text{ W}$$

$$T_{\text{on}} = 100 \text{ microseconds}$$

$$T_{\text{off}} = 10 \text{ milliseconds}$$

5 minutes of deposition onto silicon wafers gave rise to a film thickness of 210 nm.

The hydrophilicity of the deposited coatings are assessed by water contact angle measurements with a video capture apparatus (AST Products VCA2500XE) using sessile 2  $\mu\text{L}$  droplets of deionised water.

The water contact angle of coatings deposited onto polished silicon wafers is  $28 \pm 2^\circ$  confirming that they are indeed hydrophilic. The films formed were observed to be smooth and clear.

Figure 1a

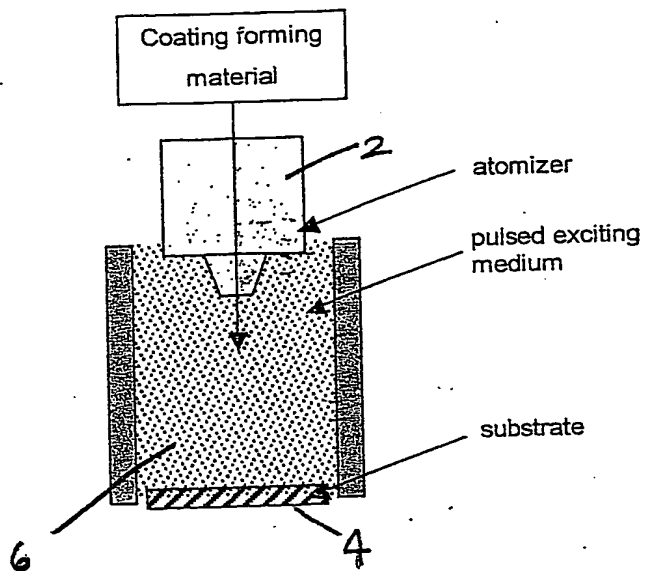


Figure 1b

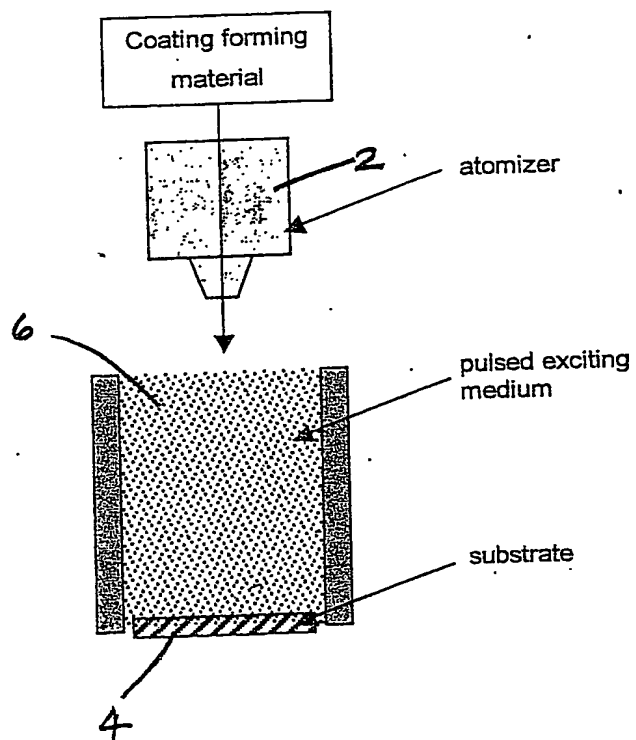


Figure 2

